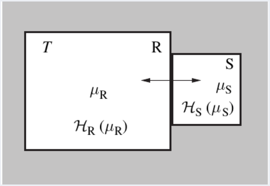
Ensambles

Lectura: M. Kardar Cap. 4; R. K. Pathria & D. Beale Caps. 3.

» Ensamble canónico

Cuando el sistema ($\mathcal{S}$) no se encuentra aislado y puede intercambia calor con un reservorio $\mathcal{R}$, la energía del sistema no es constante.



Pero $t = \mathcal{R} + \mathcal{S}$ está cerrado, y además con $E_t \gg E_\mathcal{S}$, la probabilidad de un microestado μ_t en $\mathcal{R} + \mathcal{S}$ es

$$P(\mu_\mathcal{S} \otimes \mu_\mathcal{R}) = \frac{1}{\Omega_{\mathcal{S}+\mathcal{R}}(E_t)} \Rightarrow P(\mu_\mathcal{S}) = \sum_{\mu_\mathcal{R}} P(\mu_\mathcal{S} \otimes \mu_\mathcal{R}) = \frac{\Omega_\mathcal{R}(E_t - E_\mathcal{S})}{\Omega_{\mathcal{S}+\mathcal{R}}}$$

O sea, $P(\mu_\mathcal{S}) \propto e^{\frac{1}{k_B} S_\mathcal{R}(E_t - E_\mathcal{S})}$. Desarrollo $S_\mathcal{R}$ como

$$S_\mathcal{R}(E_t - E_\mathcal{S}) \simeq S_\mathcal{R}(E_t) - E_\mathcal{S} \frac{\partial S_\mathcal{R}}{\partial E_\mathcal{R}} = S_\mathcal{R}(E_t) - \frac{E_\mathcal{S}}{T}$$

$$P(\mu_\mathcal{S}) = \frac{e^{-\beta E_\mathcal{S}}}{Z(T)}, \quad \text{con} \quad Z(T) = \sum_{\mu_\mathcal{S}} e^{-\beta E_\mathcal{S}}$$

Función de Partición Canónica

Energía Interna U

$$U = \langle H \rangle = \sum_s E_s \frac{e^{-\beta E_s}}{Z}$$

$$= -\frac{1}{Z}\frac{\partial}{\partial \beta}\sum_s e^{-\beta E_s}$$

$$U = -\frac{\partial}{\partial \beta}\ln Z$$

La energía libre de Helmholtz

$$F = U - TS \quad \Rightarrow \quad U = F + TS$$

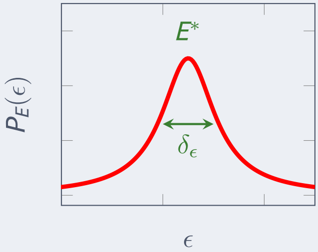
$$= F - T\frac{\partial F}{\partial T}\Big|_{N,V} = -T^2\frac{\partial}{\partial T}\left(\frac{F}{T}\right)\Big|_{N,V}$$

$$U = \frac{\partial(\beta F)}{\partial \beta}\Big|_{N,V}$$

$$-\beta F = \ln Z(T, N, \cdots) \qquad \text{Toda la Termodinámica}$$

» La distribución de probabilidad de las energías $P_E(\epsilon)$

$$P_E(\epsilon) = \sum_s P(\mu_s)\delta(E_s - \epsilon) = \frac{e^{-\beta\epsilon}}{Z}\Omega(\epsilon) = \frac{1}{Z}e^{\left[\frac{S(\epsilon)}{k_B} - \frac{\epsilon}{k_B T}\right]} = \frac{1}{Z}e^{-\beta\widetilde{F}(\epsilon)}$$



con $\widetilde{F}(\epsilon) = \epsilon - TS(\epsilon)$, ¿Quién es E^*?

$$\left.\frac{\partial\tilde{F}}{\partial\epsilon}\right|_T = 1 - T\left.\frac{\partial S}{\partial\epsilon}\right|_T \Rightarrow$$

$$\frac{1}{T} = \left.\frac{\partial S(\epsilon)}{\partial\epsilon}\right|_{T,\epsilon=E*} \Rightarrow$$

$$E^* \stackrel{?}{=} U = \int d\epsilon P_E(\epsilon)\epsilon$$ en el límite termodinámico??

¿Qué pasa con δ_ϵ^2, i.e., $\langle H^2\rangle - \langle H\rangle^2$

$$\langle H^2\rangle - \langle H\rangle^2 = \int \epsilon^2 P_E(\epsilon)d\epsilon - \left(\int \epsilon P_E(\epsilon)d\epsilon\right)^2 = \int \epsilon^2 e^{-\beta\epsilon}\frac{\Omega(\epsilon)}{Z} - \left[\int \epsilon e^{-\beta\epsilon}\frac{\Omega(\epsilon)}{Z}\right]^2$$

pero, $Z(\beta) = \int e^{-\beta\epsilon}\Omega(\epsilon)d\epsilon$

$$\frac{\partial^2 \ln Z}{\partial\beta^2} = -\frac{\partial U}{\partial\beta} = -\frac{\partial}{\partial\beta}\left[\int \epsilon e^{-\beta\epsilon}\frac{\Omega(\epsilon)}{Z}d\epsilon\right] = \int \epsilon^2 e^{-\beta\epsilon}\frac{\Omega(\epsilon)}{Z}d\epsilon + \int \epsilon e^{-\beta\epsilon}\Omega(\epsilon)\frac{\partial Z}{\partial\beta}\frac{1}{Z^2}$$

$$= \langle H^2\rangle + \frac{\partial \ln Z}{\partial\beta}\int \epsilon e^{-\beta\epsilon}\Omega(\epsilon)\frac{1}{Z} = \langle H^2\rangle - \langle H\rangle^2$$

Pero además,

$$-\frac{\partial U}{\partial\beta} = -\frac{\partial U}{\partial T}\frac{\partial T}{\partial\beta} = k_B T^2\frac{\partial U}{\partial T} = k_B T^2\ C \qquad \text{es extensivo, i.e., } \propto N$$

o sea

$$\boxed{\frac{\langle H^2\rangle - \langle H\rangle^2}{U^2} \propto \frac{1}{N}}$$

» y la $P_E(\epsilon)$, entonces?

$$P_E(\epsilon) = \frac{1}{Z} e^{\beta(S(\epsilon)T - \epsilon)} = e^{-\beta \widetilde{F}(\epsilon)}$$

Desarrollando $\widetilde{F}$ alrededor de $E^* = U$, para aproximar $P_E(\epsilon)$ por una gaussiana,

$$\begin{aligned}
\widetilde{F}(\epsilon) &= F(U) + \left.\frac{\partial \widetilde{F}}{\partial \epsilon}\right|_{\epsilon=U} (\epsilon - U) + \frac{1}{2} \left.\frac{\partial^2 \widetilde{F}}{\partial \epsilon^2}\right|_{\epsilon=U} (\epsilon - U)^2 \\
&= F(U) + 0 - \frac{1}{2} T \left.\frac{\partial^2 S}{\partial \epsilon^2}\right|_{\epsilon=U} (\epsilon - U)^2 \\
&= F(U) + \frac{1}{2T} \frac{\partial T}{\partial U} (\epsilon - U)^2 \\
&= F + \frac{1}{2TC} (\epsilon - U)^2
\end{aligned}$$

O sea,

$$P_E(\epsilon) \simeq \frac{1}{Z} e^{-\beta F} \, e^{-\frac{\beta}{2TC}(\epsilon - U)^2}$$

» Hamiltoniano Clásico

Sea un Hamiltoniano clásico $H = H(\{p, q\})$, la suma sobre microestados va con

$$d\Gamma_N = \frac{1}{N!} \prod_{i=1}^{N} \frac{d^3 q_i \, d^3 p_i}{h^3}, \quad \text{con lo cual}$$

$$Z(T) = \int d\Gamma_N \, e^{-\beta H(\{p,q\})}, \quad U = -\frac{\partial \ln Z}{\partial \beta}, \quad F = -k_B T \ln Z$$

Hamiltonianos separables

Si $H = \sum H_k$

$$Z(T) = \frac{1}{N!} \prod_k \left(\int d\Gamma_N^{(k)} e^{-\beta H_k} \right)$$

$$F = \sum_k F_k \quad \& \quad U = \sum_k U_k$$

- Sistemas no interactuantes.
- Partículas libres.
- Grados de libertad internos.

» Gas Ideal

Para un Hamiltoniano de N partículas libres no interactuantes, en $\{p_i, q_i\}$,

$$H = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m}.$$

$$Z(T,V,N) = \frac{1}{N!}\int \prod_{i=1}^{N} \frac{d^3p_i\, d^3q_i}{h^3}\, e^{-\beta \sum \frac{p_i^2}{2m}} = \frac{1}{N!}\prod_{i=1}^{N}\int \frac{d^3p_i\, d^3q_i}{h^3}\, e^{-\beta \frac{p_i^2}{2m}}$$

$$= \frac{V^N}{N!}\left[\int \frac{d^3p}{h^3} e^{-\beta\frac{p^2}{2m}}\right]^N = \frac{V^N}{N!}\frac{1}{\color{red}{\lambda(T)^{3N}}} \simeq \left(\frac{Ve}{N\lambda^3}\right)^N \quad \Rightarrow$$

$$F(T,V,N) = -k_B T \ln Z = -k_B N T\left\{\ln\left[\frac{V}{N\lambda^3}\right] + 1\right\}$$

$$U = -\frac{\partial \ln Z}{\partial \beta}$$

» Espines en un campo magnético

N espines localizados, no interactuantes, que pueden orientarse arbitrariamente, $E = \sum_{i=1}^{N} E_i = \sum_i \boldsymbol{m}_i \cdot \boldsymbol{H} = -\mu_0 H \sum_i \cos\theta_i$. La función de partición es

$Z_N(\beta) = [Z_1(\beta)]^N$

$$Z_1(\beta) = \int_0^{2\pi} d\phi \int_0^{\pi} e^{\beta\mu_0 H \cos\theta} \sin\theta \, d\theta = 2\pi \int_{-1}^{1} e^{\beta\mu_0 H x} dx = \frac{2\pi}{\beta\mu_0 H}\left(e^{\beta\mu_0 H} - e^{-\beta\mu_0 H}\right)$$

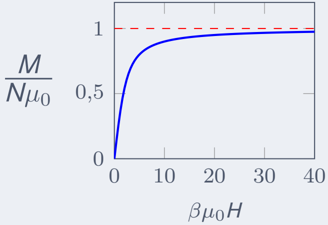
$$= \frac{4\pi}{\beta\mu_0 H} \sinh \beta\mu_0 H$$

¿y la magnetización media $M = N\langle \mu_0 \cos\theta \rangle$?

$$M_z = \frac{N}{\beta} \frac{\partial}{\partial H} \ln Z_1 = -\frac{\partial F}{\partial H}\bigg|_T$$

» Espines en un campo magnético (Cont.)

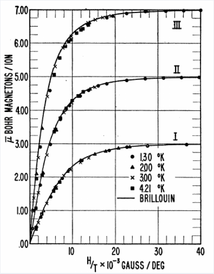
$$\frac{M}{N} = \langle \mu_0 \cos\theta \rangle = \mu_0 \left[\coth(\beta\mu_0 H) - \frac{1}{\beta\mu_0 H} \right]$$



Si $\beta\mu_0 H \ll 1$ (altas T),

$$M = N\frac{\mu_0^2}{3}\beta H$$

$$\chi_T = \lim_{H\to 0} \left.\frac{\partial M}{\partial H}\right|_T \simeq N\frac{\mu^2}{3k_B T} = \frac{\text{Cte}}{T} \qquad \text{Ley de Curie}$$



[W.E Henry, 1952]